BOSTON UNIVERSITY

GRADUATE SCHOOL

THESIS

REDUCING AGENTS IN VOLUMETRIC ANALYSIS

WITH SPECIAL REFERENCE TO

STANNOUS PERCHLORATE

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INTRODUCTION

The processes of Volumetric Analysis may be grouped into three classes, as Neutralization processes, such as that between Sodium Hydroxide and Hydrochloric Acid; Precipitation processes, such as that between Sodium Chloride and Silver Nitrate; and Oxidation-Reduction processes, such as that between Ferrous Chloride and Potassium Permanganate. Some authors, however, group the first two types together as those in which no change in valence takes place, as opposed to the remaining class in which there are always at least two such changes.

Neutralization processes were among those first developed in Analytical Chemistry as in 1839[1] we find Potassium Carbonate recommended as a primary standard; thus some progress must have been made already in this direction. Lunge[2] in 1878, proposed the substitution of Methyl Orange, an artificially prepared dyestuff, in place of the various natural extracts previously used, thus initiating a technical development which has only recently been completed by the work of Clark[3] and others. Hildebrand's[4] introduction of the Hydrogen electrode in 1913 for use in titration furnished another means of obtaining the endpoint. As a result of the present high development of these colorimetric and potentiometric methods to all sorts of neutralizations, it is doubtful whether we may expect much further

1. Ure, Dictionary of Arts, (1839)
2. G. Lunge, Ber. 11, 1944 (1878)
3. W. M. Clark, The Determination of Hydrogen Ions (1928)
4. J. H. Hildebrand, J. Am. Chem. Soc., 35, 869 (1913)

progress in that direction.

The idea of Volumetric Precipitating processes probably originated with Gay-Lussac[5] for in 1828 he suggested a method of determining Sulfate with a Barium Solution, and in 1832 published the method for Silver determination which bears his name.[6] Numerous procedures have been suggested since that time, but up to the present very few have been found of any value, principally due to the difficulty of obtaining the correct endpoint, by means of the indicators available. While theoretically conductometric methods of obtaining it could be used at present little has been accomplished. It is probable that the recent work of Fajans[7] and Hassel involving the use of "absorption" indicators will open up a broad field for the further advancement of this type of Volumetric Analysis.

By far the largest number of Volumetric processes are included in the third group, since many of our commonly determined elements are capable of variable valence or of combining with other elements which possess this property. It might seem that by this method the compounds of any two elements of variable valence could be used as the necessary oxidizing and reducing materials. The exact choice of materials is limited, however, by the necessity of choosing them with regard to proper oxidation potentials[*] as well as to the practical avoidance of

5. J. L. Gay-Lussac, Ann. chim. phys., 39, 352 (1828)
6. J. L. Gay-Lussac, Instruction sur l'essai des matieres d'argent par la voie humide. (1832)
7. K. Fajans and O. Hassel, Z. Elektrochem., 29, 495 (1924)
*. See Chapter I

errors such as would result from the use of unsuitable indicators or to the occurance of side reactions.

Dupasquier[8] in 1840 carried out the first method involving oxidation and reduction when he titrated Iodine with Sulfurous Acid. Schwarz[9] in 1853 introduced the use of Sodium Thiosulfate along with the Iodine, and since that time the applications of these useful solutions have been increasing constantly. Later other well known oxidizing agents such as Potassium Permanganate, Potassium Bichromate, Potassium Iodate, and Potassium Bromate were introduced as well as Oxalic Acid, Arsenious Acid, Ferrous and Stannous salts which are reducing agents. While in Starch we have a suitable indicator for the Iodine-Thiosulfate reaction, we had until recently none for the others, except for the Permanganate, which acts for its own indicator.

With the application of potentiometric methods as recommended by Hildebrand[*] and the development of suitable oxidation-potential indicators by Clark[10] other materials have been developed, as for example, in the recent work of Willard[11] with Ceric salts; and in all probability the next few years will see many others.

It is the purpose of this investigation to first consider

8. Dupasquier, Ann. chim. phys., 73, (1840)
9. Schwarz, Anleitung sur Massanalyse. (1853)
*   See Ref. 4 page 1
10. W. M. Clark and others, Pub. Health Reports
    38, 443 (1923) 38, 666 (1923) etc.
11. H. H. Willard, J. Am. Chem. Soc., 50, 1222, 1334,
    1368, 1372, 1379, (1928)

the general principles underlying the use of Volumetric re-
ducing agents in general, second to summarize the advantages
of, and objections to, those commonly used at present, and
third to investigate the possibilities for the use of Stannous
Perchlorate in this direction.

Chapter I

OXIDATION-REDUCTION POTENTIALS

For many years it has been conceded that oxidizing and reducing agents of various strengths exist. In the more elementary text-books, we read that Chlorine is a strong oxidizing agent while Hydrogen Peroxide, for example, is a weak one. Some of these books include a list of oxidizing (and reducing) agents in the order of their respective strengths, but until the past few years there was a noticeable lack of similarity in these lists. Books on Analytical Chemistry were even worse as the authors of them either neglected the matter entirely or else passed over it with a few generalities, they, apparently, being unacquainted with the accumulated data of Electro-Chemistry and its possible applications to oxidation-reduction processes.

Blasdale[12] in 1917 inserted a few paragraphs in his text, but it was not until the publication, in Germany, of Muller's[13] book that any real attempt was made in this direction. In 1924 Popoff[14] brought out the first book in this country which included any adequate discussion of these principles as applied to analytical problems. This was followed by that of Fales[15] in 1925, and the first of the Furman[16] translations of the works

12. W. C. Blasdale, Prin. of Quant. Anal. (1917)
13. E. Muller, Die Eletrometriche Massanalyse. (1923)
14. S. Popoff, Quant. Anal. (1924)
15. H. A. Fales, Inorg. Quant. Anal. (1925)
16. I. M. Kolthoff, Potentiometric Titrations (1926)
   Translated by Furman

of Kolthoff in 1926, since which time this material has been included in all of the up-to-date text-books on the subject.

Theory

It is universally accepted that the usual rules of equilibrium can be applied to all such oxidation and reduction reactions as are reversible.[17] When we consider that in terms of our modern electrical theory of matter, oxidation is merely a loss of one or more electrons, while reduction is a corresponding gain, we may consistently write, for example, the oxidation of Ferrous ions as follows

$$Fe^{++} \rightleftharpoons Fe^{+++} + e \tag{1}$$
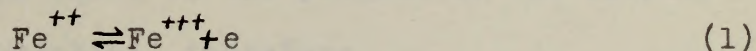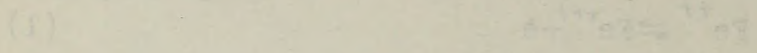
and calculate the equilibrium constant to be

$$\frac{(Fe^{+++})(e)}{(Fe^{++})} = K \tag{2}$$

or as a general case for the reaction

$$Red \rightleftharpoons Ox + ne \tag{3}$$
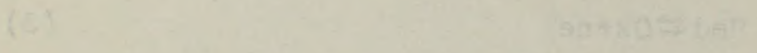
if we let (Ox) represent the concentration of the substance in its higher state of oxidation, (Red) the concentration of the substance in its lower state of oxidation, n the number of electrons involved, and (e) the so-called "electron concentration", we obtain the general equilibrium constant

$$\frac{(Ox)(e)^n}{(Red)} = K \tag{4}$$

In such reactions as include a change in the Hydrogen ion concentration, this raised to the proper power, must also be included in the numerator.

17. H. S. Taylor, Treatise on Phys. Chem., II, 843 (1925)

According to Clark[*], an inert electrode contains free electrons and to their concentration we can give a value A, a constant for any electrode system. If this electrode is dipping into a solution of an oxidizing or reducing agent in which the electron concentration has a value (e), the work done W in transferring one faraday from a concentration A to a concentration (e) is

$$W = RT\ln \frac{A}{(e)} \tag{5}$$

where R and T have the values given below.

But this work is also equal to the product of the faraday and the electrode potential, therefore

$$W = EF = RT\ln \frac{A}{(e)} \tag{6}$$

Solving this expression for E, we obtain

$$E = \frac{RT}{F}\ln \frac{A}{(e)} \tag{7}$$

where E = Potential of the electrode(in volts)

R = The gas constant(in joules)

T = The temperature(in degrees Kelvin)

F = 96,500 coulombs(one faraday)

A = A constant(see above)

(e) = The "electron concentration"

ln = Natural logarithm

This equation can be simplified by assuming a temperature of 18 degrees Centigrade and substituting the proper values,

* See reference 10, page

and the following form obtained.

$$E = A' - .058\log(e) \tag{8}$$

Where A' is a constant, log refers to logarithm to the base ten, and the other terms have the same meaning as in (7). Solving equation (4) for (e) we obtain

$$(e) = \sqrt[n]{\frac{(Red)}{(Ox)} K} \tag{9}$$

Substituting this value for (e) in (8), we obtain

$$E = A' - \frac{.058\log K}{n} - \frac{.058}{n}\log\frac{(Red)}{(Ox)} \tag{10}$$

and, for the special case where (Red) is equal to (Ox), the third term drops out giving

$$E = A' - \frac{.058\log K}{n} = E_O \tag{11}$$

where E_O is the Normal potential of the system as given in the literature.[18] Substituting this value back in (10) gives

$$E = E_O - \frac{.058}{n}\log\frac{(Red)}{(Ox)} \tag{12}$$

which is the general form of the equation desired. However, if the reaction includes a change in the Hydrogen ion concentration as below

$$Red \rightleftharpoons Ox + ne + mH \tag{13}$$

the equilbrium constant will obviously be

$$\frac{(Ox)(e)^n(H)^m}{(Red)} = K \tag{14}$$

When this is solved for (e), substituted in (8) as above

18. R. Gerke, Chem. Rev., 1, 377 (1925)

we obtain

$$E = E_o - \frac{.058}{nF} \log\frac{(Red)}{(Ox)(H)^m} \tag{15}$$

Application

During an actual titration we have a reduction of one substance going on at the same time as we have an oxidation of a second substance. This can be written (if n is one)
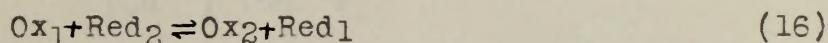
$$Ox_1 + Red_2 \rightleftharpoons Ox_2 + Red_1 \tag{16}$$

where Ox_1 is the oxidizing agent and Red_2 the reducing agent. Applying the usual equilibrium conditions, we obtain

$$\frac{(Ox_2)(Red_1)}{(Red_2)(Ox_1)} = K \tag{17}$$

and since at the equilibrium point, the two oxidation potentials must be equal

$$E_{o_1} - .058 \log\frac{(Red_1)}{(Ox_1)} = E_{o_2} - .058 \log\frac{(Red_2)}{(Ox_2)} \tag{18}$$

solving this expression we obtain

$$\log K = \frac{E_{o_1} - E_{o_2}}{.058} \tag{19}$$

By substituting the values of the Normal Potentials in this equation, we are able to obtain the ratios of the reacting substance at their equivalence point, and from this to predict the extent to which the reaction has gone. Two illustrations will probably show this a little more clearly.

First considering the reaction between Stannous ions and Cupric ions to give Stannic ions and Cuprous ions.
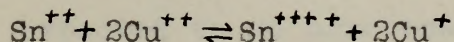
$$Sn^{++} + 2Cu^{++} \rightleftharpoons Sn^{++++} + 2Cu^{+}$$

In this case, n is two

$$\log K = \frac{2(E_{o_1} - E_{o_2})}{.058}$$

$$\log K = \frac{2(.138 - .18)}{.058}$$

$$K = .722$$

$$\frac{(Cu^+)^2 (Sn^{++++})}{(Cu^{++})^2 (Sn^{++})} = K$$

but at the equivalence point

$$\frac{(Sn^{++++})}{(2Cu^+)} = \frac{(Sn^{++})}{(2Cu^{++})} \quad \text{or} \quad \frac{(Cu^+)}{(Cu^{++})} = \frac{(Sn^{++++})}{(Sn^{++})}$$

therefore substituting in the above equation

$$\frac{(Cu^+)}{(Cu^{++})} = \sqrt[3]{K} = .896$$

or the reduction of the Cupric ions could not be quantitatively accomplished by the Stannous ions.

But, by applying the same line of reasoning to the reaction between Stannous ions and Ferric ions,

$$Sn^{++} + 2Fe^{+++} \rightleftharpoons Sn^{++++} + 2Fe^{++}$$
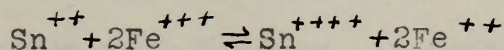
we find that

$$\log K = \frac{2(.138 - .714)}{.058}$$

$$K = 3 \times 10^{20}$$

and

$$\frac{(Fe^{++})}{(Fe^{+++})} = \sqrt[3]{K} = 6.7 \times 10^6$$

or as far as can be calculated from this principle, this reaction can be expected to go practically to completion.

While from these considerations, we can predict that a reduction or an oxidation will proceed quantitatively in the reverse case "one should never fail to test the theoretical deductions experimentally, and should not be content merely with the result of the computations"[19]

Measurement

Every titration cell contains two electrodes and the solution which is being titrated. The measured voltage of the cell is the algebraic difference of the actual potential differences between the two electrodes and the solution. One of these electrodes is known as the indicator electrode, since it acts as an indicator for the substance, or substances the potential of which it is desired to measure; the other is known as the reference electrode since its potential is constant. In this particular case the tenth-normal Calomel electrode was used as the reference electrode. This consists of a layer of Mercury, covered by a paste of Mercurous Chloride intimately mixed with Mercury, in contact with a solution of Potassium Chloride, containing 7.455g. in a liter of distilled water which has been previously saturated with Mercurous Chloride.(Fig. 1) This electrode has a potential of 0.609 volts referred to the Normal Hydrogen electrode. The indicator electrode used was merely a short piece of bright Platinum wire which had been fused into the end of a piece of glass tubing.(Fig. 2)

19. I. M. Kolthoff, Volumetric Analysis, I, 115 (1928)

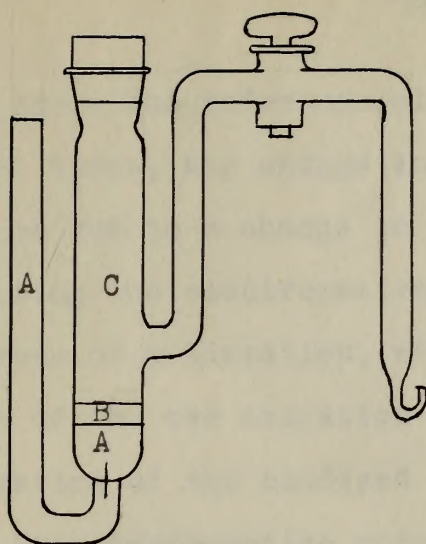Figure 1

Calomel Electrode

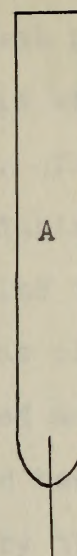Figure 2

Platinum Electrode

A   Mercury

B   Mercury-Calomel Paste
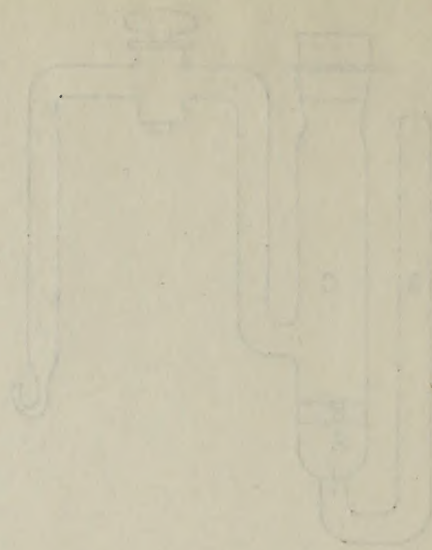
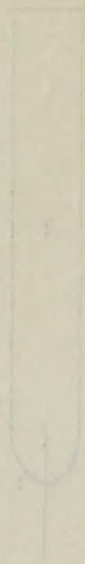C   Tenth Normal Potassium

      Chloride Solution

Figure 2

Platinum Electrode

Figure 1

Chlor-I Electrode

A   Mercury

B   Mercury-Calomel Paste

C   Peaty-Normal Potassium

     Chloride Solution

Since the reference electrode has a constant potential
at all times, any change in the measured voltage of the cell
must be due to a change in the solution itself. Thus by
measuring the electromotive force of the cell during the
progress of a titration, we are able to determine the vari-
ation of the two oxidation potentials due to the change in
the ratios of the oxidized states to the reduced states.

The electromotive force of such a cell can best be
measured by the use of a potentiometer, since by the use of
a voltmeter, too much current would be drawn from the cell
and electrolysis would result. The principle of the potentio-
meter can be explained as follows. If a source of electro-
motive force be connected to the ends of a wire AB, of uni-
form resistance, the drop in potential along the wire will
be uniform also. If now a second source of electromotive
force, weaker than the first, be connected to A and through
a galvanometer to a slider on this wire in such a way that
they are opposing each other, and this slider is moved to
some point C, so that no deflection is shown by the galvano-
meter, the voltage of the first source will be to the voltage
of the second source as AB/AC, since the potential drop be-
tween A and C is proportional.to the length.

For practical purposes it is preferred to first balance
the potentiometer using a standard cell against one of unknown
but constant value, and then substitute the cell which it is
desired to measure in place of the standard cell. This can

be better understood by reference to the following diagram,[20] which shows the complete circuit including the potentiometer, battery, standard cell, galvanometer, switch, keys, and protective resistance, the electrodes of the cell being connected to the positions marked E.M.F.
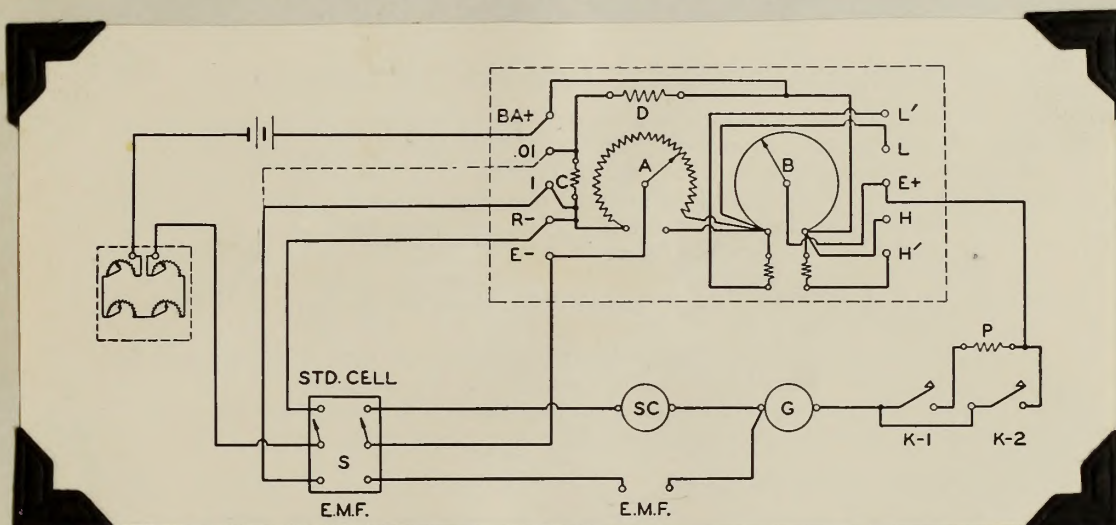
Fig. 3

The potentiometer is first standardized against the standard cell SC by throwing it in by means of the switch S, and putting sufficient resistance in the battery circuit to give no deflection in the galvanometer G when the key K-2 is tapped, provided that the potentiometer contacts A and B have been first set to read the voltage of the standard cell. The switch S is then thrown in the opposite direction so as to put the unknown cell in circuit, the contacts A and B are then moved until the circuit is again balanced as shown by

20. Leeds and Northrup, Bulletin #765 (1926)

no deflection in the galvanometer G when key K-2 is tapped, and the reading of the positions of A and B is the voltage of the unknown cell. The key K-1 is in series with the protective resistance P and is used in obtaining an approximate balance, before using the other key.

The apparatus used in this investigation was as follows
Leeds and Northrup Student's Potentiometer
Leeds and Northrup 4-Dial Resistance Box
Leeds and Northrup Portable Pointer Galvanometer
Eppley Standard Cell, 1.01880 Volts
The electrodes described previously, D. P. D. T. Switch,
tapping keys, protective resistance, and two dry cells.

no deflection in the galvanometer G when key K-2 is tapped, and the reading of the positions of A and B is the voltage of the unknown cell. The key K-1 is to serve with the protective resistance P and is used in obtaining an approximate balance, before using the other key.

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Leeds and Northrup Student's Potentiometer

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Eppley Standard Cell, 1.01830 Volts

The electrodes described previously, D. . . C. . P. Switch, tapping keys, protective resistance, and two dry cells.

Chapter II

THE COMMON REDUCING AGENTS

Ferrous Salts

The first reducing solution usually prepared in elementary quantitative analysis is a Ferrous salt, either the simple Sulfate or the double Ammonium Sulfate. The reason for this primacy can not be due to its importance since a review of the literature of Analytical Chemistry shows only four methods, all indirect, which are of any importance. The method of Blair[21] for Chromium in which the ore is oxidized by means of Sodium Peroxide to a Chromate, acidified, treated with a measured volume of the standard Ferrous solution, and the excess determined by titrating with standard Potassium Dichromate, is generally considered the standard method for that element. Treadwell[22] however, prefers to perform this analysis iodometrically. Lunge's[23] method for the estimation of Manganese Dioxide in which the sample is treated with an excess of Ferrous salt in Sulfuric Acid, and the excess determined by the titration with Potassium Permanganate, has been replaced by the method of Fresenius and Mohr[24] in which Oxalate is substituted for the Ferrous salt in spite of the possible dehydrating effect of Sulfuric Acid.

In certain steel works laboratories, Manganese in the

21. A. H. Low, Tech. Meth. of Ore Anal. 9th Ed. 74 (1922)
22. F. H. Treadwell, Quant. Anal. 4th Ed., 675 (1915)
23. G. Lunge, Chem.-Techn. Untersuchungsmethodik, 6th Ed., 569 (1913)
24. A. H. Low, Tech. Meth. of Ore Anal. 9th Ed., 142 (1922)

steel(or iron) is determined by oxidizing it, using either
the Bismuthate or the Persulfate method and reducing the
resulting Permanganic acid with Ferrous[25] salt. As this
procedure is now included in Method of Testing A-33-24
(when Chromium is absent) of the American Society of Testing
Materials, it may be considered as of some importance.

The fourth use of a Ferrous solution is for the deter-
mination of Vanadium in Ferro-Vanadium by the standard method
of the American Vanadium Co.[26] In this method, after both the
Iron and Vanadium have been oxidized by Permanganate, an
excess of a Ferrous solution is added, and the latter deter-
mined with standard Bichromate solution.

Treadwell also mentions the method of LeBlanc and
Eckhardt[27] for the determination of Persulfates by the use of
Ferrous solution while Scott seems to prefer this to Oxalic
Acid method of Kempf.[28]

Possibly this lack of procedures involving the use of
Ferrous salts is largely influenced by their lack of stability.
While it is generally considered that Ferrous salts are un-
stable, practically no work has been done in order to ascertain
the conditions necessary for maximum stability.

25. S. Popoff, Quant. Anal., 2nd Ed., 499 (1927)
26. W. W. Scott, Stan. Meth., 4th Ed., 142 (1922)
27. LeBlanc and Eckhardt, Chem. News, 81, 38 (1900)
28. R. Kempf, Ber., 38, 3963 (1905)

Oxalic Acid and Oxalates

In 1882, Zimmerman[29] investigated the reactions between Permanganate and Oxalic Acid in both Hydrochloric and Sulfuric acid solution and came to the conclusion that the reaction took place quantitatively above 70 degrees centigrade. During the next twenty years, a few chemists used Oxalic Acid as a reducing agent, but it was not until about 1903 when Sorenson[30] finished his researches on the Sodium salt that bears his name that it replaced Iron wire as the common means of standardizing Permanganate solutions. As a result of this reaction Oxalic Acid or acidified Oxalate is commonly used in many cases of indirect analysis of oxidizing agents, the excess being titrated with Permanganate.

Among these are the Fresenius-Mohr* method for Manganese Dioxide mentioned previously and the similar methods of Lux[31] for Lead Dioxide and red lead. In the presence of a Manganese Salt and Nitrate, Nitric Acid reacts with Oxalic Acid[32] quantitatively, and Debourdeaux[33] similarly used Oxalic Acid to determine Chlorates, Bromates and Iodates. Kempf worked out the method for the analysis of Persulfates** by means of Oxalic Acid in the presence of Silver Sulfate as a catalyst mentioned previously.

29.   Zimmerman, Ann. 213,305 (1882)
30.   S. P. L. Sorenson, Z. anal. Chem. 42,513 (1903)
 *.   See Ref. page 15
31.   Lux, Z. Anal. Chem, 19,153 (1880)
32.   I. M. Kolthoff, Vol. Anal. II, 338 (1929)
33.   Debourdeaux, Compt. rend., 136, 1668 (1903)
**.   See Ref. 28, page 16

In passing two other methods involving the reducing action of Oxalic Acid should be mentioned. One of these that of Luckow[34] in which Calcium(from a soluble salt) is precipitated as Oxalate, and Oxalate subsequently titrated is very satisfactory. The second, that of Kolthoff[35] for organic substances in which the substances are oxidized to Oxalate in alkaline solution which in turn is oxidized with Permanganate, is as yet of limited usefulness.

The stability of Oxalic Acid solutions has been investigated as long ago as 1898 by Jorissen[36] who found that it was slowly oxidized to water and Carbon Dioxide when exposed to the light. Later it was found that it also decomposed somewhat with the formation of Carbon Monoxide as well. Kolthoff[37] however, found that a tenth normal solution did not change even after a year if kept in the dark.

Arsenious Acid

Arsenious Acid has been in use as a reducing agent at least since 1852, when Penot[38] published his method for the determination of Hypochlorites. This is the well-known method used to evaluate the "available Chlorine" of bleaching powder in which the active material is extracted with water and an aliquot portion is titrated with standard Arsenious Acid until a drop of the solution does not turn Potassium

34. Luckow, Z. anal. Chem., 26, 9 (1887)
35. I. M. Kolthoff, Vol. Anal. II, 339 (1929)
36. W. P. Jorissen and H. F. Izn, Z. anal.Chem., 23, 726 (1910)
37. I. M. Kolthoff, Vol. Anal. I, 239 (1928)
38. Penot, Bull. Soc. Ind. de Mulhouse, 118 (1852)

Iodide starch paper blue. Scott[39] gives an improved method in which Potassium Iodide is added and the liberated Iodine titrated directly.

Arsenious Acid in a Sodium Bicarbonate solution is frequently used to standardize Iodine[40] solution, and, according, to Gyory[41] in Hydrochloric Acid solution to standardize Bromate solutions. Pyrolusite and certain Peroxides which can liberate Iodine by Bunsen's distillation method[42] can also be determined much better with Arsenious Acid according to Lunge-Berl[43] than by the use of the usual Thiosulfate. Feit[44] makes use of the ability of Arsenious Acid in alkaline solution to reduce Mercuric salts to metallic Mercury as a means of analyzing such salts, byt apparently other methods are preferred. Since Arsenious Acid is not affected by Persulfate it has become the preferred solution in the determination of Manganese in steel by the Persulfate[45] method and is frequently substituted on account of its greater stability for a Ferrous Salt in the Bismuthate[46] method for that element.

It is probable that many other uses might be found for this reducing agent, but since we can in most cases get as satisfactory results with Sodium Thiosulfate, one which

39. W. W. Scott, Stand. Meth. of Chem. Anal., 155 (1927)
40. S. Popoff, Quant. Anal. 2nd Ed., 156 (1927)
41. G. Gyory, Z. anal. Chem., 32, 415 (1893)
42. F. B. Treadwell, Quant. Anal. 4th Ed , 661 (1915)
43. G. Lunge-Berl, Chemisch-Technische Untermethoden 7th Ed., 972 (1921)
44. W. Feit, Z. anal. Chem., 28, 318 (1889)
45. G. v. Knorre, Z. angew. Chem., 14, 1149 (1901)
46. H. A. Fales, Inorganic Quant. Anal., 338 (1925)

directly or indirectly covers a much broader field, little progress will probably be made in that direction in the immediate future.

Titanous salts

The availability of Titanous salts was suggested by Ebelman[47] in 1847, who showed that they were capable of reducing quantitatively the salts of Copper and Iron. In 1876, Glatzel[48] published an article on this subject, but it was not until 1903, when Knecht[49] started his intensive investigations on these solutions that any serious attention was paid to them. Anyone reading the well-known monograph of Knecht and Hibbert[50] might well imagine that here we have the ideal and universal reducing agent. According to this book, a Titanous solution will react quantitatively with the salts of Iron and Copper, Chromium, Tin, Tungsten, Molybdenum, Vanadium, Lead, Manganese, Cobalt, in addition to Hydrogen Peroxide, Chlorates, Perchlorates, Persulfates, Nitrates, Hydrosulfates and Sulfates, numerous types of organic compounds, including many common dyestuffs, and can even be used to determine the degree of mercerization of cotton.

In spite of these claims Titanous salts are rarely used in most analytical laboratories. Treadwell lists only three methods involving the use of Titanous Chloride, the method of

47. Ebelman, Ann. chim. phys., 20, 385 (1847)
48. E. Glatzel, Ber., 9, 1829 (1876)
49. E. Knecht, Ber., 33, 1550 (1903)
50. E. Knecht and E. Hibbert, New Red. Meth. in Vol. Anal. 2nd Ed., (1925)

Knecht and Hibbert for Ferric Iron in which a direct titration
is made using a Thiocyanate indicator, the same authors' method
for the determination of Hydrogen Peroxide, a direct titration,
and their indirect method for the determination of Persulfates
using a Ferric salt. Scott gives only the modification of
Thornton and Chapman[51] for the iron determination and mentions
no other use. Kolthoff also includes this method and adds the
various methods for determining Cupric Copper and recommends a
new procedure for the analysis of organic nitro compounds.[52]

Probably the chief reason for the failure of Titanous
salts to be used more generally is due to their lack of sta-
bility. When exposed to the air both the Chloride and Sulfate
take up oxygen and rapidly lose their reducing strength.
There is also a photo-chemical reduction in which the Titantic
salt and Hydrogen is formed. In order to overcome the first
of these difficulties a particular form of apparatus must be
used in conjunction with the burette so that the solution is
at all times exposed to an atmosphere of hydrogen. The second
can be somewhat overcome by not exposing the solution to sun-
light, but even with these precautions the solution must be
frequently standardized.

Sodium Thiosulfate

As before mentioned[*], Sodium Thiosulfate has been in con-
stant use as a reducing agent practically since the beginning

51. E. Knecht and E. Hibbert, New Reduction Meth. in
     Vol. Anal. 2nd Ed., (1925)
52. I. M. Kolthoff and C. Robinson, Rec. Trav. Chim.,
     46, 169 (1926)
 *. See Ref. 9 page

of modern Volumetric analysis. At present it is probably our most valuable substance for that purpose since the reaction between it and Iodine is one of the most accurate of all titrations, and the necessary Iodine can be liberated when a soluble Iodide is treated with practically any substance possessing oxidizing properties. There is, of course, a slight titration error introduced by the use of the Starch indicator, but according to Kolthoff[53] at ordinary temperatures it does not amount to more than one half of a cubic centimeter of one thousandth normal solution under the usual conditions of Iodide in concentration, temperature and volume. Due to the reaction between Alkalies and Iodine and other interfering reaction, the pH of the solution should be less than 7.6 for a solution which is tenth normal in Iodine and still less for more dilute solutions.

The method for the determination of Iodine involves nothing more than dissolving it in a strong Iodide solution diluting and titrating directly with standard Thiosulfate adding the Starch when only a small amount of the Iodine remains. If a solution of an Iodate in the presence of excess of Iodide is acidified free Iodine is quantitatively formed which can then be determined as in the preceding case. Kjeldahl[54] made use of this same reaction a means of determining acid in his original method for Nitrogen, but altho Groger,[55]

53. I. M. Kolthoff, Vol. Anal. II, 351 (1929)
54. J. Kjeldahl, Z. anal. Chem., 22, 366 (1883)
55. M. Groger, Z. angew. Chem., 3, 353 (1890)

Schwarz[56] Moody[57] and many others have studied this reaction this method has not displaced the usual basic titration.

Chlorine, Bromine, Dichromates, Permanganates, Ferri-Cyanides, Chlorates, Bromates, Hydrogen, Peroxides, Periodates, Persulfates, Pentavalent Arsenic and Antimony, Vanadate, Ferric Iron, Cupric Copper, Cobalt, Cerium, and Molydic Acid can be determined by treatment with an excess of Potassium Iodide and the subsequent titration of the Iodine with Thiosulfate. Pyrolusite, Lead Dioxide, Telluric Acid, and similar substances can be determined by treatment with Hydrochloric Acid, catching the liberated Chlorine in an Iodide solution, followed by the usual titration.

During the last thirty years, many attempts have been made to develop analytical methods for the anlysis of various organic compounds. Among the most important of these are two which involve the use of Thiosulfate. The first of these, the determination of the "Iodine Number" a measuring of the unsaturation of an oil or fat, consists of allowing a solution of Iodine Chloride[58] or Iodine Bromide[59] to react with the substance adding Potassium Iodide and the usual titration with Thiosulfate. A blank run at the same time and in the same manner furnishes a means of calculating the amount of Halogen absorbed. The other method of Kopperschaar[60] for Phenol,

56. H. Schwarz, Monatsh., 19, 139 (1898)
57. S. E. Moody, Z. anorg. Chem., 46, 423 (1905)
58. J. J. A. Wijs. Z. anal. Chem., 37, 277 (1898)
59. J. Hanus, Z. Untersuch. Nah., 913 (1901)
60. W. Kopperschaar, Z. anal. Chem., 15, 233 (1876)

consists in treating the Phenol with Potassium Bromate and Bromide, acidifying and titrating the excess Bromine by adding Iodide and Thiosulfate.

Sodium Thiosulfate solutions as ordinarily prepared are made from boiled water[61] and allowed to stand for several days before standardizing as otherwise the solution is not sufficiently stable, but gains in strength. It has generally been thought that since the boiling of the water removed Carbon Dioxide, it was the resulting formation of Thiosulfurous Acid followed by its breakdown into Sulfurous Acid and free Sulfur that caused this change. This idea is also strengthened by the fact that if a small amount of Sodium Carbonate or Hydroxide is added the stability is greatly increased. Recently Mayr[62] has found that this change is partly due to the presence of so-called Thio-bacteria, which have the ability to decompose Thiosulfates, but he could not find a substance capable of hindering their action.

61. S. Popoff, Quant. Anal. 2nd Ed., 161 (1927)
62. Mayr, Z. anal. Chem., 68, 274 (1926)

Chapter III

STANNOUS SALTS as REDUCING AGENTS

Practically the only Stannous salt which has been used as a reducing agent is the Chloride, if we may except those cases where the Sulfate is formed in solution as the result of the addition of Sulfuric Acid. Each of the suggested methods for the use of Stannous Chloride in Volumetric Analysis will be taken up and its desirability considered in each case. In a later chapter, the possibilities for the use of the Perchlorate in those cases where it might be of value will be considered.

The best known method involving the use of Stannous Chloride is the Zimmermann-Reinhardt[63] for the determination of Iron. In this method, Ferric Chloride is reduced with Stannous Chloride, while hot, using the color change as the equivalence point, cooling, diluting, removing the excess with Mercuric Chloride, and finally titrating the reduced Iron with standard Potassium Permanganate or Potassium Bichromate. This method is of great importance and is in constant use wherever this element is determined. Its chief source of difficulty seems to be the recognition of the color change when the correct amount of Stannous Chloride has been added. If too much is added, there will be a precipitation of Mercury in the next step, which completely ruins the analysis. It has been

63. Cl. Zimmermann and C. Reinhardt, Chem. Ztg., 13, 160 (1884)

claimed that the precipitated Mercurous Chloride reduces the

Ferric Chloride[64] formed in the titration, but, if only a

slight excess of Stannous Chloride was added, this effect

is so small as to be negligible. This method differs from

those which follow as in it the Stannous Chloride is not

used as a titrating solution.

Fresenius,[65] in 1886, took a previous qualitative test,

and developed it into a quantitative method for the deter-

mination of Ferric Iron with Stannous Chloride. In this method

the Iron as Ferric Chloride is titrated with Stannous Chloride,

while hot, until it becomes colorless. As stated previously,

this change in color is not a sharp one, so for analytical

purposes it is desirable to run over the end-point and back

titrate with a standardized Iodine solution. Due to the rapid

change in the reducing power of the Stannous solution, it is

necessary to compare it with the Iodine solution at the same

time that the Iron is being determined.

Scott[66] gives a modification of this method for small

amounts of Iron, using a much weaker solution and performing

the actual titration rapidly in a casserole to better observe

the end-point. He also describes a rather complicated arrange-

ment of apparatus for the purpose of preventing oxidation of the

solution, by the use of which it is claimed, that it is not nec-

essary to standardize oftener than once every ten or fifteen days.

64. C. Meincke, Z. Offentl. Chem., 4,433 (1898)
65. W. Fresenius, Z. anal. Chem., 25,160 (1886)
66. W. W. Scott, Stand. Meth. 4th Ed., 260 (1927)

Schimpf[67] includes a method for the determination of
Mercuric Chloride among the uses of Stannous Chloride, which
he refers to as the method of Laborde. This method consists
of titrating a solution of the Mercuric Chloride, the pH of
which has been accurately adjusted by a mixture of Acetic
Acid and Ammonium Acetate, with the Stannous solution until
a brownish color is obtained. The Stannous Chloride previously
must have been standardized by titrating samples of known
purity. While this author includes it as if it were of some
importance, no references to such a method could be found
elsewhere in the various books on Analytical Chemistry.

Muller and Gorne[68] have collected the available methods
which could be used for the determination of Stannous Chloride,
as well as those in which it is the standard solution itself,
and investigated them potentiometrically, publishing their
results in an article with the title "Potentiometriche
Stannometrie." By the use of the potentiometer he was able to
eliminate the color change as a source of error, as well as to
increase the accuracy of the methods to some extent. He found
that he could obtain satisfactory results when Stannous
Chloride reacted with Ferric Chloride, Iodine, Potassium
Permanganate, Potassium Bichromate, and Mercuric Perchlorate.
He was unable to obtain any results with Potassium Ferricyanide,
and not very satisfactory ones with Gold and Platinum in the

67. H. W. Schimpf, Ess. of Vol. Anal. 4th Ed., 231 (1925)
68. E. Muller and W. Gorne, Z. anal. Chem., 73,385 (1928)

form of their complex Chlorine Acids. In a later paper, with

Bennewitz,[69] he published more of his work with these two latter

substances, but further improvements will have to be made

before these methods will be useful.

Stannous Chloride solutions, like those of Titanous and

Ferrous salts, are very unstable. When it is desired that the

reducing value of the solution should remain constant, it is

necessary to take precautions to prevent oxidation. Among

those recommended are the keeping of the solution under an

atmosphere of Hydrogen from a Kipp generator, and the use of

yellow Phosphorous or Pyrogallic Acid for the purpose of

removing the Oxygen from the air. As all of these require

bulky and complicated pieces of apparatus, the oxidation of

Stannous Chloride has been investigated by several workers,

but thus far no definite recommendations have resulted from

their efforts.

69. E. Muller and R. Bennewitz, Z. anorg. Chem., 179,
    113 (1929)

Chapter IV
STANNOUS PERCHLORATE

A very extensive survey of the literature revealed but two references to this substance, one by Noyes and Toabe[70] who prepared it, in solution, as a preliminary to their investigation of the electrode potential of Stannous Tin, and a second by Prytz[71] who made use of it during an investigation of the hydrolysis of the Stannous salts.

The most obvious method of preparation of this substance is to treat Tin with Perchloric Acid. Tin, in various forms, was treated with Perchloric Acid of various strengths, but in no case was an appreciable amount of the metal dissolved after four or five hours of continued heating. Letters were then written to two men who had worked on Perchlorates for possible information not otherwise available. Dr. G. F. Smith of the University of Illinois replied that he had never prepared any of this salt, but that he would try to do so. In a later letter he stated that very fine turnings would react slowly if heated with 70% Perchloric Acid. Dr. Stephen Popoff of the State University of Iowa suggested the treatment of Stannous Chloride with Silver Perchlorate. As none of the latter substance was available, this method could not be tried out.

Due to the non-volatility of Perchloric Acid, it seemed

70. A. A. Noyes and K. Toabe, J. Am. Chem. Soc., 39, 1537 (1917)
71. M. Prytz, Z. anorg. allgem. Chem., 172, 147 (1928)

reasonable to expect that if Stannous Chloride was evaporated
with it, Stannous Perchlorate would result and Hydrogen Chlo-
ride would be given off. Several attempts to do this were
made, but in every case yellowish muddy suspensions were
obtained before the fumes of Perchloric Acid started to come
off. A qualitative test with Silver Nitrate solution showed
considerable Chloride present so this method was abandoned.

It was suggested that the salt could be made by the re-
action between Stannous Hydroxide and Perchloric Acid. All
the available samples of Stannous Chloride were dissolved in
Hydrochloric Acid, and carefully neutralized with Sodium Hy-
droxide solution. The resulting precipitate was filtered
and washed with warm water, but after numerous(in one case
seventeen) washings, the material still contained Chlorides.
As a result, this method was abandoned, also.

Noyes and Toabe[*] had worked out an indirect method which
they found to be successful. This method consisted of first
forming Cupric Perchlorate by treating Cupric Oxide with the
acid, and then displacing the Copper by Tin to form the Stan-
nous salt. After a few preliminary experiments, this proce-
dure was followed, but the resulting solution had a brownish
scum and gave a very decided test for Iron. After obtaining
Copper Oxide and Tin of better grade, carefully distilling
the water, and carrying out the displacement in a closed con-
tainer, a satisfactory material(in solution) was obtained.

*. See Ref. 70, page 29

The following method was finally used. 32 grams of Copper Oxide were added to 110cc. of 60% Perchloric Acid(sp.gr. 1.54) which had previously been diluted to 400cc. and the mixture heated to boiling. In a short time, a clear blue solution was obtained, which was then cooled and poured into a glass stoppered bottle of about 450cc. capacity, containing 100g. of 60 mesh Tin. This was shaken vigorously by hand, for fifteen minutes, and then occasionally during the next two days, but allowed to stand tightly stoppered during the interval between shakings. By the morning of the fourth day, no test for Copper could be obtained with Ammonium Hydroxide, so the solution was filtered thru glass wool into a bottle containing Tin. An attempt to substitute mechanical stirring resulted in a rather dirty turbidity which was probably due to the presence of very finely divided Copper or Tin. In a few days a yellow coloration developed, but as the authors of this method had found this to have no undesirable effect, this was not considered detrimental. This solution when first prepared was 2.08 Normal and since the volume was 390cc. the yield, based on the Cupric Oxide, was practically quantitative. All solutions used in titrations were prepared by merely diluting this solution to the desired strength.

It was originally intended that this substance should be substituted for the Chloride, so, as the chief drawback to the latter is its lack of stability, experiments intended to

measure the stability of the Perchlorate in the usual strengths used in analysis were made. At the same time solutions of the Chloride were measured similarly.

The first method which was tried was an attempt to measure the absorption of the Oxygen by the change in pressure in a closed flask by means of a Mercury manometer. It was found that both solutions absorbed the gas at a very rapid rate, so great, in fact, that no satisfactory quantitative results could be obtained.

A method making use of the change of electromotive force caused by the oxidation was then substituted. After a number of preliminary measurements were made, three sets of values were obtained which resembled each other enough to be compared. The average of each reading is given in Table I, and the data is plotted in Fig. 4. From these results, it can be seen that the stability of the Perchlorate is not much, if any, better than that of the Chloride.

In the meantime, a series of experiments were carried out in order to ascertain if Stannous Perchlorate possessed any particular properties which would make it desirable as a reducing agent. Each one of these will be considered in the following pages.

TABLE I

COMPARATIVE STRENGTHS

of

STANNOUS PERCHLORATE and STANNOUS CHLORIDE

As Determined from Measurements of Electromotive Force

Time in Hours	E. M. F. in Volts			
	Perchlorate		Chloride	
	1.0 N	0.1 N	1.0 N	0.1 N
0.0	.0284	-.0450	.0425	-.0636
0.5	.0336	-.0407	.0445	-.0515
1.0	.0445	-.0190	.0515	-.0404
2.0	.0477	-.0111	.0548	-.0190
3.0	.0534	.0000	.0547	-.0138
4.0	.0562	.0195	.0674	.0000
5.0	.0618	.0210	.0727	.0307
6.0	.0663	.0210	.0746	.0304
7.0	.0614	.0241	.0733	.0324
24.0	.0630	.0210	.0862	.0325

The Tenth Normal Calomel and bright Platinum electrodes were used for these determinations. The same electrodes were used for all solutions.

FIGURE IV

E.
M.
F.
in
V
o
l
t
s

N Sn(ClO$_4$)$_2$

N SnCl$_2$

0.1N Sn(ClO$_4$)$_2$

0.1N SnCl$_2$

COMPARATIVE STABILITIES
Sn(ClO$_4$)$_2$ vs SnCl$_2$

TIME in Hours

0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7

0   1   2   3   4   5   6

FIGURE IV

0.7

0.6

0.5

0.4

0.3

0.2

E.

M.F.

0.1

0.0

in

V

-0.1

o

l

-0.2

t

-0.3

s

-0.4

-0.5

-0.6

-0.7

N Sn(ClO$_4$)$_2$

N SnCl$_2$

0.1N Sn(ClO$_4$)$_2$

0.1N SnCl$_2$

COMPARATIVE STABILITIES

Sn(ClO$_4$)$_2$ vs SnCl$_2$

0   1   2   3   4   5   6

TIME in Hours

USE IN THE ZIMMERMANN-REINHARDT METHOD*

A solution of Stannous Perchlorate was substituted for
the usual Stannous Chloride as a reducing agent for the
Iron. Due to the yellowish color of the Perchlorate solution,
the sharp color change at the end-point could not be observed.
A Ferric solution of known strength was then treated with a
slight excess of Stannous Perchlorate, in the usual manner,
but, after cooling and diluting, upon addition of the required
quantity of Mercuric Chloride, none of the desirable silky
precipitate was obtained, but a dirty brown one instead. After
three attempts using less excess of the Perchlorate which gave
similar results, it was decided that this substance could not
be used for this purpose.

* See Ref. 63, page 25

USE AS A QUALITATIVE REAGENT

Most of the modern systems of Qualitative Analysis
determine the presence of Mercuric Mercury by its reaction
with Stannous Chloride. In this test a white precipitate
of Mercurous Chloride is first formed, which in the presence
of an excess of the Stannous salt, darkens rapidly due to the
further reduction to metallic Mercury.

A solution of the Perchlorate was prepared of the same
strength as that of the usual Chloride solution, but upon
being added to a solution of Mercurous Chloride, the white
precipitate first formed dissolved instead of darkening,
probably due to the oxidizing power of the Perchloric Acid
present. It would seem that from this behavior, that the
Perchlorate is not suitable for use as a qualitative
reagent.

Table II

STANNOUS PERCHLORATE vs IODINE

Procedure:-25cc. of Iodine solution(.09588N) was diluted to 400cc. with distilled water, Perchloric Acid(20%) was added, and titrated with an approximately 0.1N solution of Stannous Perchlorate. The course of the reaction was followed by the potentiometer using the electrodes previously described.

Volume added in cc.	E. M. F. in volts		
	5cc. Acid	8cc. Acid	10cc. Acid
0	.3640	.3618	.3546
5	.3470	.3429	.3424
10	.3325	.3315	.3295
15	.3172	.3179	.3164
20	.3014	.2950	.2754
23	.2837	.0301	.0234
25	.0087	.0153	.0123
27	.0000	.0096	.0085
30	-.0107	.0036	.0050
35	-.0153	-.0050	.0020
40	-.0177	-.0086	-.0062

Remarks:-In all three concentrations of acid, an end-point was obtained at practically 23.0cc., as shown by the color change and the drop in potential. The color of the Starch was reddened by the solution.

Conclusion:-Stannous Perchlorate reduces Iodine quantitatively.

Figure V

$Sn(ClO_4)_2$ vs I_2

10cc Acid

8cc Acid

5cc Acid

cc of $Sn(ClO_4)_2$ Added

Volts

Figure Ⅵ

$2w(10^4)z$ as T

cc of $2w(10^4)z$

10cc Acid

cc Acid

5cc Acid

5cc Acid

V.P.eV

Table III

STANNOUS PERCHLORATE vs POTASSIUM PERMANGANATE

Procedure:-25cc. of Potassium Permanganate solution(.0819N) was diluted to 400cc. with distilled water, Sulfuric Acid (1.84) was added, and titrated with an approximately 0.1N solution of Stannous Perchlorate. The course of the re-action was followed by the potentiometer using the elec-trodes previously described.

Volume added in cc.	E. M. F. in Volts		
	5cc. Acid	8cc. Acid	10cc. Acid
0	.8947	1.0640	1.0041
5	.9784	1.0450	1.0218
10	.9391	1.0140	1.0218
15	.9391	1.0000	1.0221
20	.8939	.9982	1.0206
23	.8766	.9982	1.0206
25	.7885	.9801	1.0206
27	.4000	.5104	.6040
30	.0680	.2203	.3502
35	.0662	.2114	.3230
40	.0628	.2125	.3230

Remarks:-In all three cases, the color change came at 27.2 and the drop in potential immediately thereafter.

Conclusion:-Stannous Perchlorate reduces Potassium Perman-ganate quantitatively.
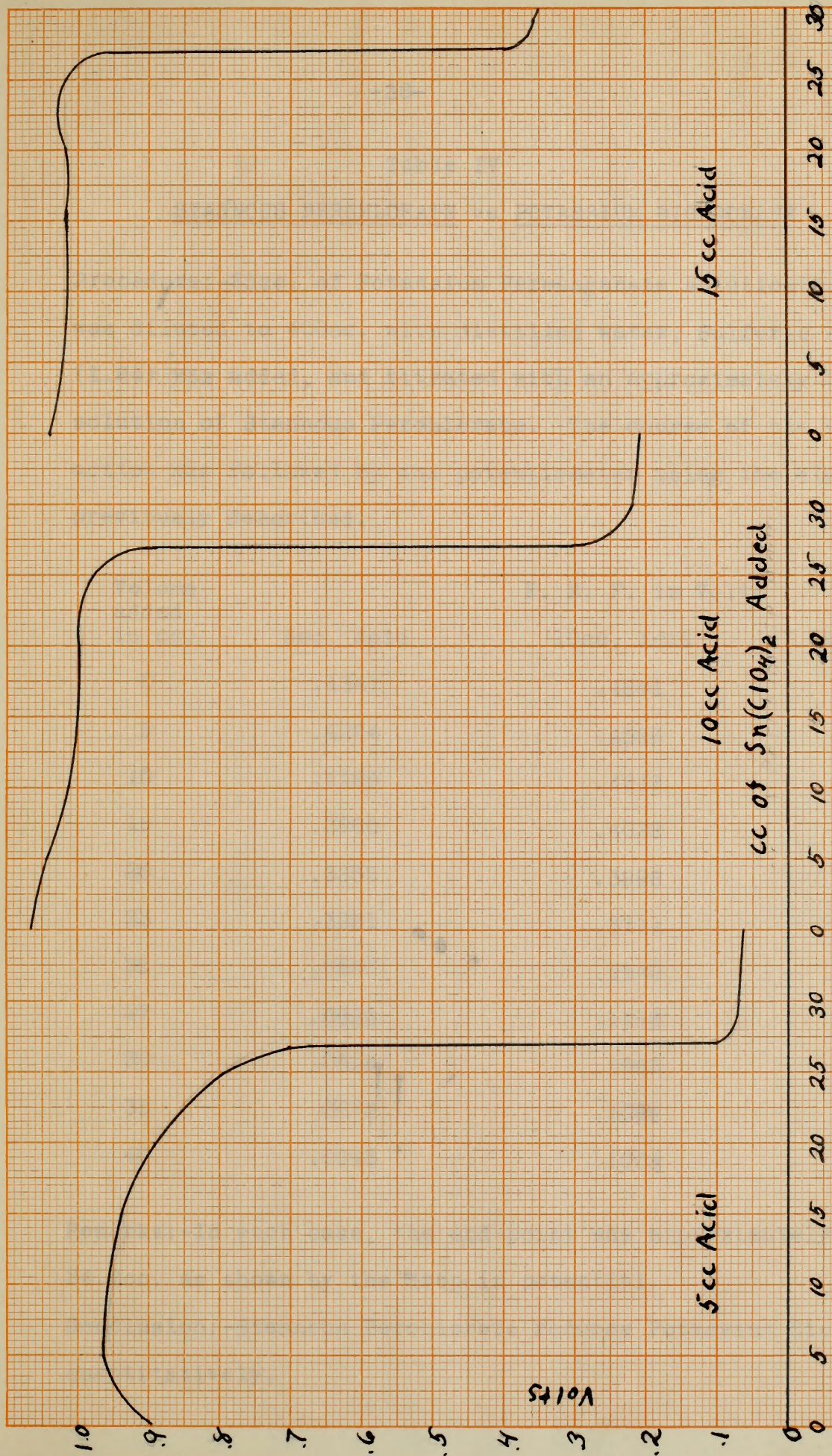
Figure VI

$Sn(ClO_4)_2$ vs $KMnO_4$

5 cc Acid

10 cc Acid

15 cc Acid

cc of $Sn(ClO_4)_2$ Added

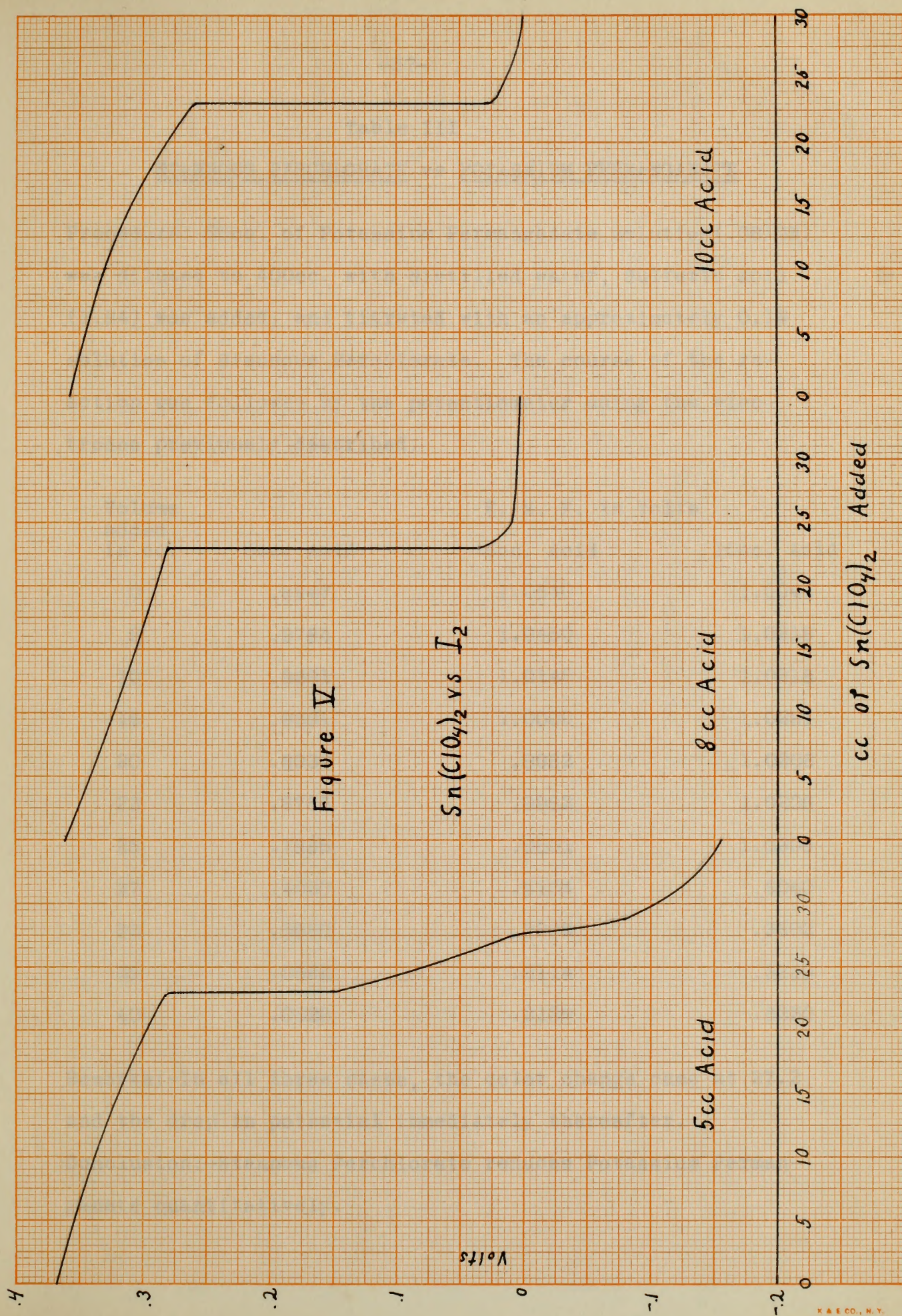Volts

Sn(ClO4)2 vs K(OH)4

Figure XI

Table IV

STANNOUS PERCHLORATE vs POTASSIUM BICHROMATE

Procedure:-25cc. of Potassium Permanganate solution(0.100N) was diluted to 400cc. with distilled water, Sulfuric Acid (1.84) was added, and titrated with an approximately 0.1N solution of Stannous Perchlorate. The course of the reaction was followed by the potentiometer using the electrodes previously described.

Volume added in cc.	E. M. F. in Volts		
	5cc. Acid	10cc. Acid	15cc. Acid
0	.4341	.4841	.5730
5	.4274	.4588	.5626
10	.4169	.4316	.5577
15	.3900	.4028	.5326
20	.3855	.3898	.4094
23	.3251	.3111	.3055
25	.0680	.1130	.0703
27	.0638	.1116	.0619
30	.0618	.1092	.0440
35	.0672	.1088	.0319
40	.0643	.1008	.0327

Remarks:-In each case, the end-point was approximately at 24.7cc. as shown by the drop in potential.

Conclusion:-Stannous Perchlorate reduces Potassium Bichromate quantitatively.

Figure VII

Sn((ClO4))2 vs K2Cr2O7

5 cc Acid

10 cc Acid

15 cc Acid

cc of Sn((ClO4))2 Added

Volts

Figure XIV

Sn(ClOH)₃ vs N₃ Cr₂ O₇

Picric Acid

10cc Acid

Picric Acid
Sn(ClOH)₂ ?.0cc

Picric Acid

8410V
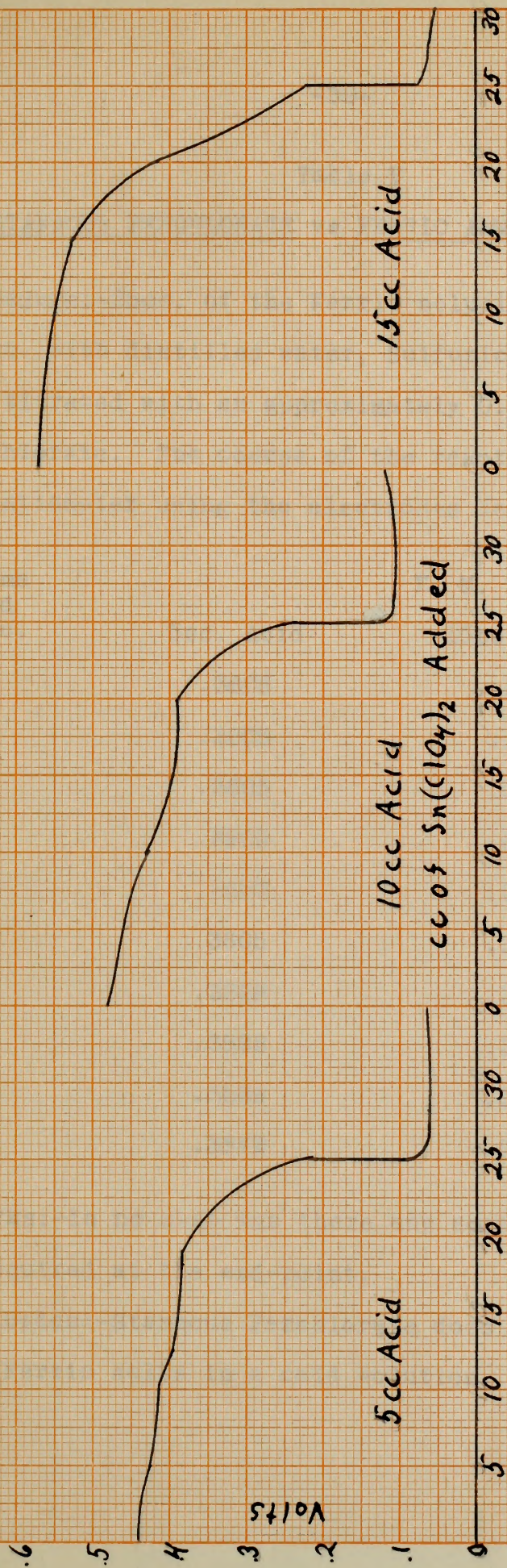
Table V

STANNOUS PERCHLORATE vs FERRIC AMMONIUM SULFATE (Cold)

Procedure:-25cc. of the Ferric solution(1.0) was diluted to
400cc. with distilled water, Sulfuric Acid(1.84) was added,
and titrated with an approximately 0.1N solution of Stannous
Perchlorate. The course of the reaction was followed by the
potentiometer using the electrodes described previously.

Volume added in cc.	E. M. F. in Volts		
	5cc. Acid	10cc. Acid	15cc. Acid
0	.3605	.3752	.3786
5	.3605	.3733	.3685
10	.3605	.3729	.3662
15	.3605	.3710	.3668
20	.3605	.3671	.3668
23	.3605	.3670	.3635
25	.3588	.3590	.3635
30	.3588	.3485	.3635
35	.3588	.3328	.3326
40	.3572	.3063	.3000

Remarks:-in no case was there any apparent change in potential
as required at the end-point.

Conclusion:-Stannous Perchlorate does not react quantitatively
with Ferric salts in a cold solution.

Volts

0.4

0.3

0.2

0.1

0

5 cc Acid

5 10 15 20 25 30 0

10 cc Acid

5 10 15 20 25 30 0

15 cc Acid

5 10 15 20 25 30

cc of $Sn(ClO_4)_2$ Added

Figure VIII

$Sn(ClO_4)_2$ vs $FeNH_4(SO_4)_2$ (Cold)

Zn(ClO4)2 vs FeNH4(SO4)2 (cont.)

Figure XIII

cc of Zn(ClO4)2 added

15 cc Acid

10 cc Acid

5 cc Acid

2110 V

Table VI

STANNOUS PERCHLORATE vs FERRIC AMMONIUM SULFATE (Hot)

Procedure:-25cc. of the Ferric solution(0.1N) was diluted to 400cc. with distilled water, Sulfuric Acid(1.84) was added, and heated to boiling, titrated with an approximately 0.1N solution of Stannous Perchlorate. The course of the reaction was followed by the potentiometer using the electrodes previously described.

Volume added in cc.	E. M. F. in Volts		
	5cc. Acid	8cc. Acid	10cc. Acid
0	.5912	.6064	.6304
5	.3908	.3000	.4114
10	.3644	.3000	.3968
15	.2344	.3835	.3753
20	.2242	.3674	.3514
23	.2240	.3680	.3307
25	.2091	.3535	.3295
27	.2111	.3607	.3142
30	.2000	.3535	.2925
35	.1880	.3454	.2838
40	.1994	.3258	.2818

Remarks:-In each case it was necessary to titrate and read the potential very rapidly in order that the solutions might not cool off.

Conclusion:-Stannous Perchlorate does not react quantitatively with Ferric salts in a hot solution.
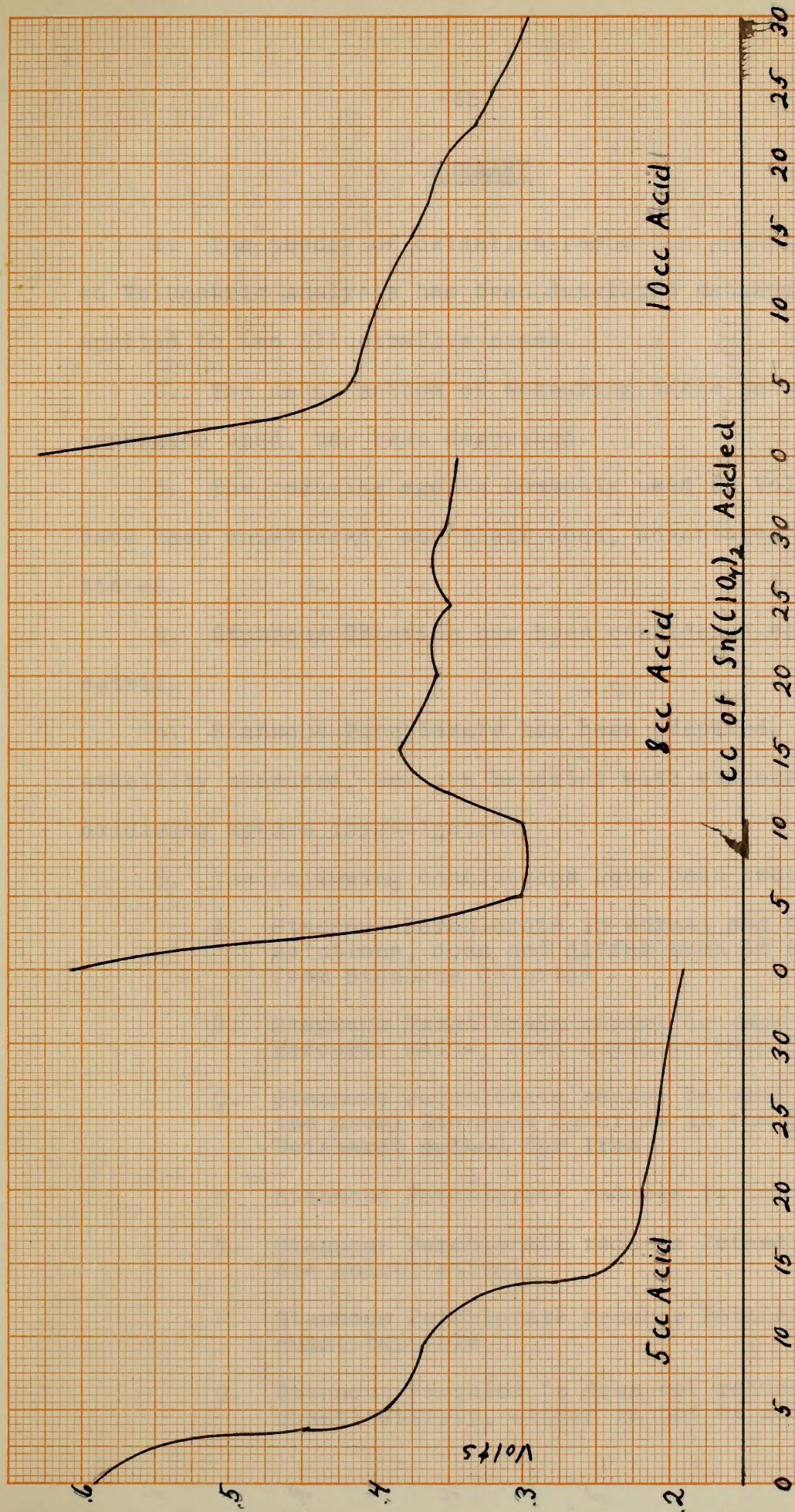
Figure IX

$Sn(ClO_4)_2$ vs $FeNH_4(SO_4)_2$ (Hot)

cc of $Sn(ClO_4)_2$ Added

10cc Acid

8cc Acid

5cc Acid

Volts

Figure IX

10 cc Acid

25 cc Acid

Adding 5w(ClO₃)₂ of 5%

Zw(ClO₃)₂ HNH(CO₃)₂ vs Zw(ClO₃)₂ (Hot)

SUMMARY

1. The theory of oxidation-reduction potentials as related to Volumetric Analysis has been developed mathematically, and applied to two illustrative cases.

2. The usual method of measuring these potentials, and the apparatus used, has been described.

3. The reducing agents commonly used in Volumetric Analysis have been considered, and their uses, advantages and objections stated.

4. Stannous Chloride has been considered somewhat more in detail.

5. Stannous Perchlorate has been prepared, its comparative stability measured, and its behavior with various commonly used oxidizing agents investigated.

6. The following conclusions have been reached:

    A. Stannous Perchlorate in normal and tenth normal solutions, does not differ much in stability from Stannous Chloride

    B. Stannous Perchlorate cannot be used to test for Mercuric salts, even qualitatively

    C. Stannous Perchlorate cannot be used in place of the usual Stannous Chloride in the Zimmermann-Reinhardt method for Iron

    D. Stannous Perchlorate reduces Iodine quantitatively

    E. Stannous Perchlorate reduces Potassium Permanganate quantitatively

    F. Stannous Perchlorate reduces Potassium Bichromate quantitatively

    G. Stannous Perchlorate does not reduce Ferric salts quantitatively, either in hot or cold solution

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ABBREVIATIONS

All abbreviations used in the above bibliography and in the
foot notes are authorized abbreviations adopted as standard by
the International Union of Pure and Applied Chemistry and given
in the official "List of Periodicals Abstracted", published by the
American Chemical Society in 1926.